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JES FOCUS ISSUE ON PROGRESS IN MOLTEN SALTS AND IONIC LIQUIDS

Poly(vinyl chloride) Ionic Liquid Polymer Electrolyte Based on Bis(fluorosulfonyl)Amide for Sodium Secondary Batteries

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Non-flammable electrolytes have been extensively studied to improve the safety of energy storage devices. In this study, a new ionic liquid polymer electrolyte (ILPE) prepared by a cast technique using poly(vinyl chloride) (PVC) as the host polymer was examined for sodium secondary batteries. The ILPE containing 50 wt% of 1-ethyl-3-methylimidazolium bis(fluorosulfonyl)amide [C₂C₁im][FSA] ionic liquid showed an ionic conductivity of 5.6 mS cm⁻¹ at 318 K. It remains stable up to 517 K based on 5 wt% loss. Stable sodium metal electrodeposition/dissolution was observed at the cathodic limit of the electrochemical window for the ILPE containing Na[FSA] ([C₂C₁im][FSA]:Na[FSA]:PVC = 2.0:1.0:1.0 w/w). The anodic limit was observed at around 4.7 V vs. Na⁺/Na on a Pt working electrode, while on an Al working electrode a higher anodic stability owing to passivation was observed. In the Na/[C₂C₁im][FSA]-Na[FSA]-PVC/-Na₂FeP₂O₇-cell with the theoretical capacity of 97 mAh g⁻¹, a reversible capacity of 92 mAh g⁻¹ was obtained at 363 K for the Na₂FeP₂O₇ positive electrode. These results suggest great potential of this PVC-based ILPE for constructing very safe sodium secondary batteries.

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Lithium secondary batteries are used in various applications such as portable electronics, consumer electronics, and auto motives.^{1,2} However, the uneven distribution of lithium resources might limit their feasibility in large scale energy storage systems. Consequently, sodium secondary batteries have become one of the most promising alternatives to lithium secondary batteries.³ The key advantages of using sodium-based energy storage devices are the low cost, and the abundant resources and low redox potential of sodium ($E^\circ_{\text{Na}^+/\text{Na}} = -2.71$ vs. SHE; which is ~ 0.3 V higher than $E^\circ_{\text{Li}^+/\text{Li}}$).

While organic electrolytes are currently used in researching sodium secondary batteries,^{4,5} ionic liquids (ILs) offer great advantages in terms of safety, such as low vapor pressure, low flammability, high thermal stability, high conductivity, and wide electrochemical window.^{6,7} The physical and electrochemical properties of ILs in Na secondary batteries have been studied in recent works.^{8–12} In real application, polymerization of the IL is one important technique to retain the advantages of ILs and avoid leakage. As a type of gel polymer electrolytes (GPE), the resulting “ionic liquid polymer electrolytes (ILPEs)” consists of ILs, the host polymer, and another component for electrochemical reactions (e.g. alkali metal salt).^{13,14} In ILPE, it is assumed that the IL phase is trapped within the polymer matrix, forming a self-standing polymer electrolyte with the ions moving in the liquid phase. The advantages of ILPE are high processability, high flexibility, and high dimensional stability that lead to the elimination of the separator. In comparison with the conventional separator, ILPE offers better capacity to trap liquid electrolytes,¹⁵ and acts as the separator and electrolyte at the same time.

One of the most challenging issues for ILPEs is improving the compatibility among the IL, the host polymer, and the third component (e.g. alkali metal salt). Most studies of ILPE for lithium secondary batteries are based this ternary system; using poly(ethylene oxide) (PEO) as a host polymer.^{16–21} For sodium ion conducting ILPE, only a few candidate host polymers have been demonstrated, including poly(vinylidene difluoride) (PVdF) and poly(vinylidene fluoride-hexafluoropropylene) (PVdF-HFP).^{22,23} Very recent research also focused on PEO-based ILPEs for sodium secondary batteries.^{24–27} From the fundamental viewpoint, compared to the case of Li⁺-based polymer electrolytes, a weaker interaction between Na⁺ and the host poly-

mer and the weaker ion-ion interaction may result in more efficient creation and transport of Na⁺ ions as the charge carrier.²⁸

Our recent reports showed the high potential of IL electrolytes for sodium secondary batteries in combination with various electrode materials especially at elevated temperatures.^{8,10,29–33} For secondary batteries, operation at elevated temperatures is preferable with the aid of thermally and chemically stable IL electrolytes, in many environments (such as the engine compartments of automobiles) that are constantly heated by waste heat from devices or machines. Sodium iron pyrophosphate, (Na₂FeP₂O₇ theoretical capacity: 97 mAh g⁻¹), which is composed of naturally abundant elements Na, Fe and P is an attractive positive electrode material with three-dimensional diffusion path of Na⁺.^{34–38} Particularly, it is known to provide high rate performance in the IL system of Na[FSA]-[C₂C₁im][FSA] (FSA⁻ = bis(fluorosulfonyl)amide and (C₂C₁im)⁺ = 1-ethyl-3-methylimidazolium cation).³⁹

The present study reports the physicochemical and electrochemical properties of the new ILPE system of Na[FSA]-[C₂C₁im][FSA]-PVC (PVC = poly(vinyl chloride)) including the charge-discharge behavior of the Na₂FeP₂O₇ positive electrode. Among the few reports of using PVC as a host polymer for ILPEs, Deraman et al. studied the conductivity and electrochemical properties of PVC doped with ammonium triflate IL.⁴⁰ Recently, another group tested PVC as a host polymer for two types of phosphonium ILs, [P_{14,6,6,6}][Cl] and [P_{14,6,6,6}][NTf₂] (P_{14,6,6,6}⁺ = trihexyltetradecylphosphonium cation),⁴¹ and characterized the chemical, morphological, thermomechanical, and electric properties of the resulting ILPE. The influence of ionicity of the phosphonium IL on the ionic conductivity of the PVC-based electrolyte and the thermomechanical properties of PVC was also reported in the same study. Compared to these previous studies, here we present the first report using PVC as a host polymer in ILPE based on bis(fluorosulfonyl)amide ILs for sodium secondary batteries.

Experimental

Materials.—The air sensitive materials were handled in a glove box under a dry deoxygenated argon atmosphere. The salts, Na[FSA] (Mitsubishi Materials Electronic Chemicals, water content < 30 ppm) and [C₂C₁im][FSA], (Kanto Chemical, water content < 30 ppm) were purchased and vacuum-dried at 353 K prior to use. The analytical grade PVC (average M_w 85,000, Fluka) was used as received.

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Table I. Composition of the [C₂C₁im][FSA]-Na[FSA]-PVC ILPE samples.

	Weight ratio			Fraction of [C ₂ C ₁ im][FSA] (wt%)
	[C ₂ C ₁ im][FSA]	Na[FSA]	PVC	
ILPE-1	0	1.0	1.0	0
ILPE-2	0.5	1.0	1.0	20.0
ILPE-3	1.0	1.0	1.0	33.3
ILPE-4	1.5	1.0	1.0	42.9
ILPE-5	2.0	1.0	1.0	50.0

Tetrahydrofuran (THF, Wako Chemicals) was used as supplied. Sodium iron pyrophosphate, Na₂FeP₂O₇, was synthesized according to the previous report.³⁹

Preparation of ILPE.—The ILPE films were prepared by a solution casting technique. PVC (1 g) was dissolved in 40 mL of THF, and the mixture was stirred vigorously until a clear homogenous solution was formed. The two salts of [C₂C₁im][FSA] and Na[FSA], in appropriate ratios (see Table I) were added into the solution, and stirred at room temperature for 24 hours until a transparent and homogenous solution was formed. The viscous solution was cast into a petri dish and left in open air to allow the THF to evaporate. The film was then dried under vacuum at 333 K for 48 hours to form the flexible and self-standing polymer electrolyte. All films were stored in the glove box until analysis. Attempt to prepare ILPE with a higher content of [C₂C₁im][FSA] IL (>50 wt%) resulted in segregation of the IL phase, and the film was not self-standing.

Analysis.—The ionic conductivity (σ) of the synthesized ILPEs was measured by an impedance analyzer (3520-80, Hioki E.E. Corp). The ILPE was placed between a pair of stainless steel blocking electrodes. The data were collected in the frequency range between 1.0×10^6 and 4.0 Hz with the amplitude of 10 mV at the open circuit potential. σ was calculated from the resistance of the bulk value (R_b) found in the complex impedance diagram according to Eq. 1:

$$\sigma = \frac{d}{R_b A} \quad [1]$$

The ILPE was punched into a disk with the electrode area (A) of 0.4 cm². Its thickness (d) was measured to be ~0.45 mm. Thermal decomposition of the ILPEs was analyzed by a Netzsch thermogravimetric analyzer (STA409EP) from 308 to 823 K under dry nitrogen flow at a heating rate of 5 K min⁻¹. Scanning electron microscopy (SEM) (Cambridge, Leica) was used to observe the morphology of the samples. For cross sectional views, the sample was immersed in liquid nitrogen for 180 s and mechanically divided into pieces. Differential scanning calorimetric (DSC) measurements were carried out on a DSC-8230 Thermo Plus EVO II Series (Rigaku) instrument under a nitrogen atmosphere. Samples were hermetically sealed in Al cells in a glove box and then heated from 233 to 423 K at a heating rate of 5 K min⁻¹. Cyclic voltammetry was performed in a two-electrode cell (2032-type coin cell), with the ILPE placed between Cu, Al or Pt working electrodes and the Na counter electrode. Charge-discharge test of the Na/ILPE/Na₂FeP₂O₇ cell was performed with a Bio-Logic VSP potentiostat or a Hokuto Denko charge-discharge unit (HJ1001SD8) using 2032-type coin cells assembled in an Ar-filled glove box. The positive electrode was prepared by mixing Na₂FeP₂O₇, acetylene black (AB) as a conductive additive, and polytetrafluoroethylene (PTFE) as a binder in a weight ratio of 75:20:5. The resulting sheet typically has a thickness of ~10 μ m, and pressed on Al current collector. The Na metal disc was used as negative electrode (Aldrich, purity 99.95%) and pressed onto Al current collector. The Na₂FeP₂O₇ electrode was impregnated with the ILPE in the form of THF solution prior to the cell construction, and the THF solvent was removed under vacuum.

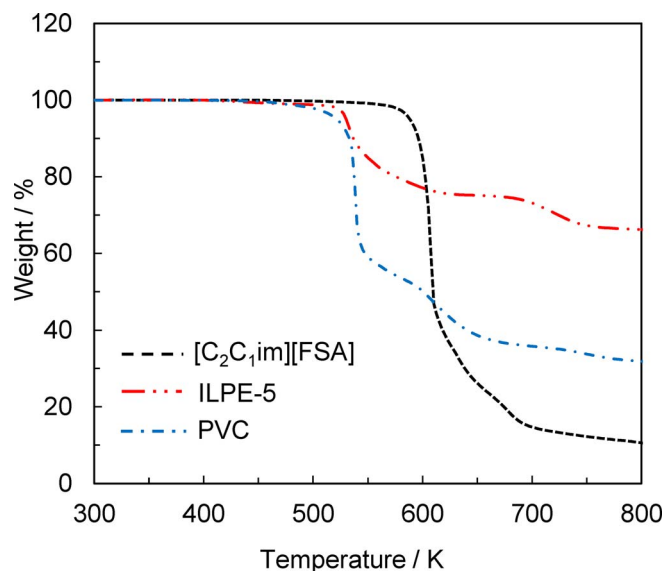


Figure 1. Thermogravimetric curves of ILPE-5, pure PVC, and the [C₂C₁im][FSA] ionic liquid. Scan rate: 10 K min⁻¹.

Results and Discussion

Thermal behavior.—Figure 1 shows thermogravimetric curves for ILPE-5 (the sample with the highest IL ratio), PVC polymer, and [C₂C₁im][FSA] IL. The decomposition temperature of ILPE-5 reached up to 517 K based on the 5 wt% loss criterion. The thermal stability of the ILPE depends on the PVC polymer, since the IL used here is more stable than the host polymer. The ILPE has sufficient thermal stability for the battery tests in the present study below 373 K.

In comparison with ILPEs using other host polymers such as PEO²⁵ or PVdF-HFP,^{42,43} the PVC-based ILPEs did not display any first-order phase transition in the temperature between 298 and 423 K according to the DSC measurements, suggesting that the IL phase remains a liquid within the host polymer network, and that the PVC host polymer retains its form. The same behavior has been observed for methyl cellulose (MC)-based polymer electrolyte.⁴⁴

Ionic conductivity.—Figure 2 shows the Arrhenius plots of ionic conductivities for the ILPEs in the temperature range between 298 and 363 K. The ionic conductivity increases with increasing amount of IL, a trend that is in good agreement with a previous study of the ILPE containing *N*-butyl-*N*-methylpyrrolidinium bis(trifluoromethylsulfonyl)amide ([C₄C₁pyrr][TFSa]) for lithium ion batteries.⁴³ The sample ILPE-1 (0 wt% IL) shows the lowest conductivity of 5.26×10^{-6} mS cm⁻¹, at 318 K, suggesting this system does not work without IL. The addition of the IL is believed to weaken the interaction between the polymer chains and hence enhance movements of the ions in the matrix. The sample with 50 wt% IL (ILPE-5) displayed the maximum ionic conductivity of 1.69 mS cm⁻¹ at 298 K. The 1.0:2.0 weight ratio of Na[FSA] and [C₂C₁im][FSA] in ILPE-5 corresponds to the molar ratio of 0.42:0.58. The ionic conductivity of the Na[FSA]-[C₂C₁im][FSA] binary IL system at this ratio is 2.6 mS cm⁻¹ at 298 K by linear approximation from a previous work.¹⁰ Comparison of these two values suggests that the ionic conductivity is reduced to 65% when the IL is packed into the polymer electrolyte. According to previous report,³⁹ the transport number of Na⁺ in the Na[FSA]-[C₂C₁im][FSA] was 0.27. By multiplying this value by 1.69 mS cm⁻¹, the Na⁺ ion conductivity in ILPE-5 is estimated to be 0.46 mS cm⁻¹ at 298 K under the assumption that the transport number does not change in the ILPE. Because of its high ionic conductivity, ILPE-5 is used for further electrochemical analysis below.

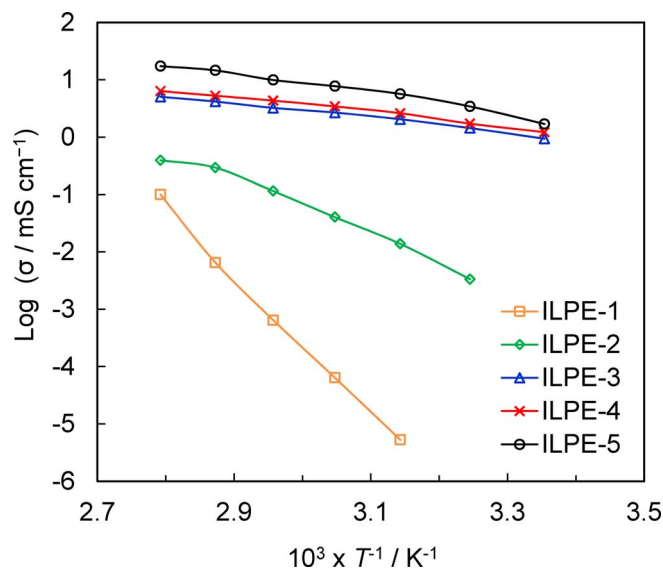


Figure 2. Arrhenius plots of ionic conductivity of the ILPEs with different ratios of $[C_2C_1im][FSA]$ ionic liquid in the temperature range between 298 and 363 K.

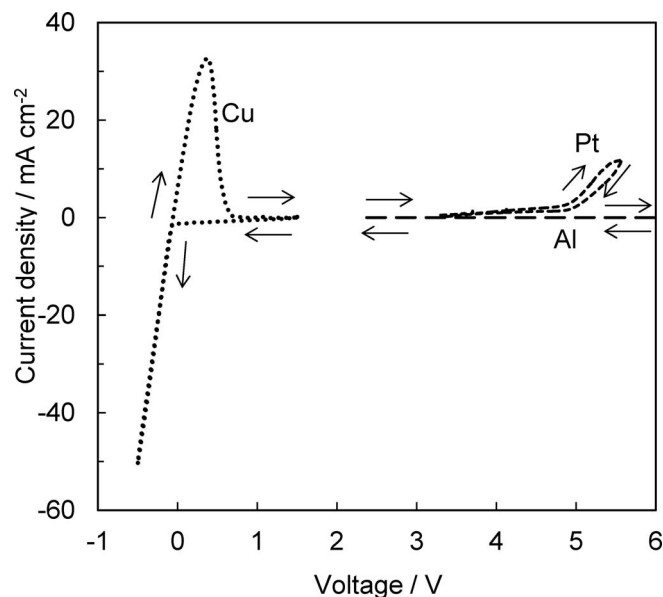


Figure 4. Cyclic voltammograms of Cu (negative potential region), Pt (positive potential region), and Al (positive potential region) plate electrodes at 363 K with the ILPE-5 electrolyte. The two-electrode test cell was used with the Na metal counter electrode. Scan rate: 5 mV s^{-1} .

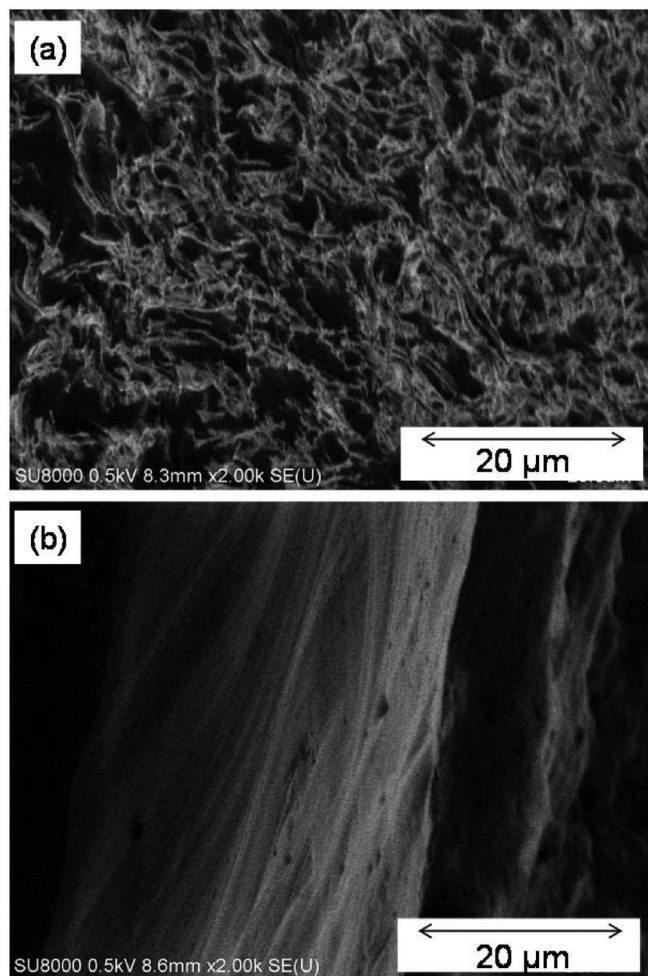


Figure 3. (a) Surface and (b) cross sectional SEM images of ILPE-5.

SEM image.—Figure 3 shows the surface and cross sectional SEM images of the ILPE-5 film. SEM observation of the ILPE sample without any special pretreatment is possible owing to the low vapor pressure of the ILs. The surface of the ILPE-5 film was rough and some inhomogeneity was observed. On the other hand, no obvious porous structure was observed in the cross sectional view suggesting homogenous impregnation of the $Na[FSA]-[C_2C_1im][FSA]$ IL into the host polymer. The inhomogeneity at the surface is attributed to the removal of the solvent, and it does not extend to the interior. A similar observation has been reported for other ILPEs.^{42,44,45}

Electrochemical window.—Figure 4 shows the cyclic voltammograms of Cu (negative potential region), Pt (positive potential region), and Al (positive potential region) plate electrodes with the ILPE-5 electrolyte at 363 K. For the $Na[FSA]-[C_2C_1im][FSA]$ IL system, it was reported that Na metal deposition/dissolution occurs at 0 V vs. Na^+/Na .¹⁰ In this experiment, the cyclic voltammogram indicates that Na metal deposition/dissolution occurs for ILPE-5 at the cathodic limit with the Coulombic efficiency of 57%. It should be noted this electrochemical reaction occurs at around -0.1 V vs. the Na metal counter electrode under the present condition. Although the deposition overpotential is observed, the dissolution should occur at or above the Na^+/Na redox potential. This observation suggests that the Na metal counter electrode only worked as a quasi-reference electrode, it did not correctly indicate the potential of the Na^+/Na redox couple, most likely owing to the surface film formation. Similar behavior was observed for the gelled IL Na^+ conductors for sodium batteries.⁴⁶ The deposition overpotential observed in the $Na[FSA]-[C_2C_1im][FSA]$ IL was not observed for this ILPE, suggesting that the interfacial process occurs more smoothly in the solid state than in the liquid state,¹² which may be related to the difference in the properties of surface film. Unfortunately, surface analysis of the Na metal electrode after cycle was difficult in this study because the bad condition of the electrode surface. The anodic decomposition occurs around 4.7 V, which is comparable to the case of the $Na[FSA]/PEO$ polymer electrolyte.²⁶ Although the voltammogram data on a flat Pt electrode provides only preliminary anodic stability, the present result indicates the possible compatibility of ILPE-5 to many of the known positive electrode materials for Na secondary batteries. The Al working electrode

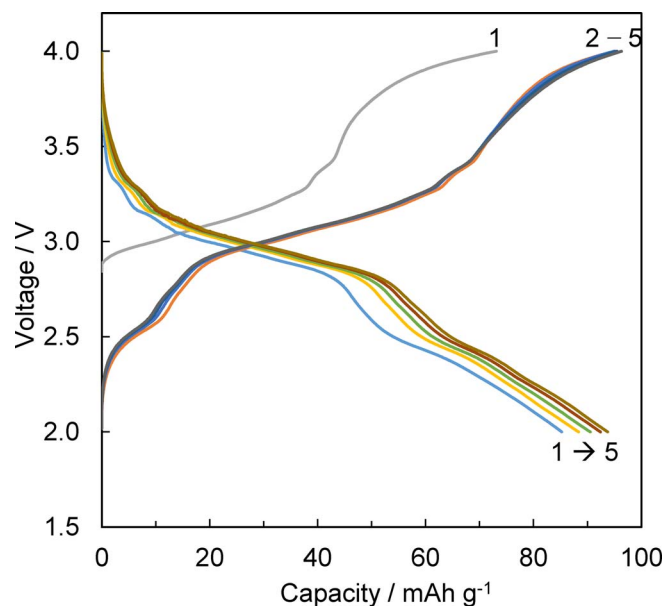


Figure 5. Galvanostatic charge-discharge curves for the Na/ILPE-5/Na₂FeP₂O₇ cell at 363 K. Cut-off voltage: 2.0–4.0 V, current density: 10 mA g^{−1}.

exhibits the highest anodic stability with ILPE-5 without showing the onset of anodic current, suggesting the validity of Al current collector for positive electrodes. This is similar to the observation for the Na[FSA]-[C₂C₁im][FSA] IL system, and indicates the formation of passivation film on the electrode surface.

Charge-discharge behavior of Na₂FeP₂O₇.—Figure 5 shows the galvanostatic charge-discharge curves of the Na/ILPE-5/Na₂FeP₂O₇ cell at 10 mA g^{−1} and 363 K. The curves show a stair-case shape with a small plateau at 2.4 V followed by a large plateau at 2.9 V. However, the plateaus are somewhat less clear compared to those in organic and IL electrolytes.^{35,39} In particular, the discharge capacity below 2.3 V is significantly larger than the charge capacity in the same voltage region. This difference seems to be supplemented in the voltage region above 3.5 V. This suggests the existence of an electrode process with large reaction resistance that is absent in the liquid system. The reversible capacity increases during the consecutive cycles and reaches 92 mAh g^{−1} at the 5th cycle, with the Coulombic efficiency of 97.3%. The increase in discharge capacity probably arises from a greater extend of the impregnation of the active materials by the electrolyte. Further cycles test was not conducted in this study since the capacity of the present cell fades immediately at a higher current density. By considering the high stability of the Na/Na[FSA]-C₂C₁im[FSA]-IL/Na₂FeP₂O₇ cell with the corresponding ionic liquid (more than 1500 cycles),³⁹ the Na/ILPE-5/Na₂FeP₂O₇ cell is potentially stable for longer cycles. Improvement in rate capability is a future problem for this system.

Conclusions

This study reported the first PVC-based ILPE [C₂C₁im][FSA]-Na[FSA]-PVC for sodium secondary batteries. Its ionic conductivity increases with the content of IL, reaching a maximum at [C₂C₁im][FSA]:Na[FSA]:PVC = 2.0:1.0:1.0 in w/w (ILPE-5). The combined thermogravimetry and differential scanning calorimetry analyses indicated that the ILPE thermally decomposes without melting at above 500 K. Stable electrodeposition/dissolution of sodium metal occurred at the cathodic limit for ILPE-5, and the anodic limit on a Pt electrode was around 4.7 V vs. Na⁺/Na. The discharge capacity of 92 mAh g^{−1} was obtained at 363 K with a Na₂FeP₂O₇ positive electrode in the Na/ILPE-5/Na₂FeP₂O₇-cell. These results suggest the

potential of the PVC-based ILPE as a solid state electrolyte for safe, reliable sodium secondary batteries.

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